学 位 論 文 要旨
Dissertation Abstract

学位請求論文（Dissertation）

Title：Study on Adsorptive Separation Processes for CH_4 Enrichment and CO_2 Recovery from Biogas

バイオガス中メタンの濃縮および二酸化炭素回収のための吸着分離プロセスに関する研究

専攻（Division）：Mechanical Science and Engineering
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学位論文要旨（Dissertation Abstract）

Biomass is an abundance material that being used as alternative resource to produce biogas nowadays. Biogas contained major composition of methane, CH_4 and carbon dioxide, CO_2. However, this gas needs a treatment to obtain high concentrated methane, CH_4 and recovery CO_2. In this study, pressure swing adsorption (PSA) and temperature swing adsorption (PSA) are being use as the method to get high recovery ratio with high concentrated gases. Zeolite 13X, high silica zeolite (HSZ) and carbon molecular sieve (CMS) are being selected to be packed in the adsorption column as the adsorbent. Due to biogas contain water vapor, the research is focusing on influence of water vapor for both methods, PSA and TSA. Experiments are carried out with variables cycle times, desorption pressure, water vapor content in the feed gas and regeneration flow rate. By comparing the results obtained at dry and humid condition, it was obviously proven that the composition of product and desorption outlet gas were affected by humidity feed gas. In this experiment, CMS adsorbent is not critically affected by the influence of water vapor. However, pre-dehumidification must be essential to improve concentration and recovery of CH_4 in the product gas.

学位論文要旨（Dissertation Abstract）

The biomass fuel is said to be carbon neutral. However, carbon dioxide of the biomass fuel origin must be controlled now. Post-combustion carbon and biogas separation technologies have been developed around the world. The most common technologies are pressure swing adsorption (PSA) and temperature swing adsorption (TSA). PSA is considered to be more expensive due to the high energy consumption and big vacuum pump for making the vacuum condition. On the other hands, size of the conventional TSA process tends to become large because long time is necessary for heating and the cooling of the adsorption column. Both processes are experimentally investigated to get high separation performance for biogas. Zeolite 13X, high silica zeolite (HSZ) and carbon molecular sieve (CMS) are selected as CO_2-adsorbents and packed in the adsorption column. In special, influence of water vapor contained in the feed gas was focused. Among the employed adsorbent, CMS is the most hydrophobic.

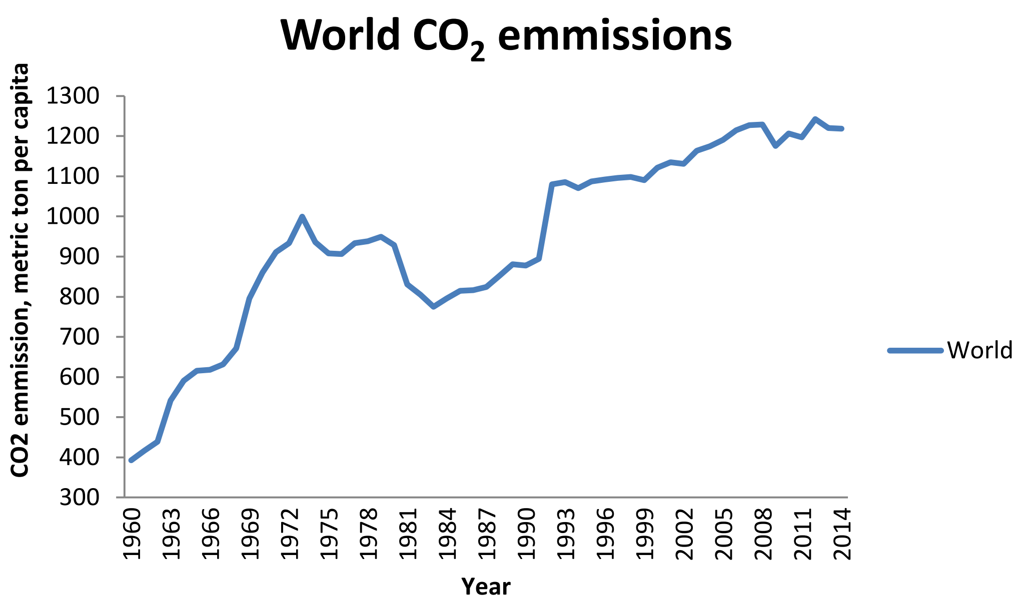
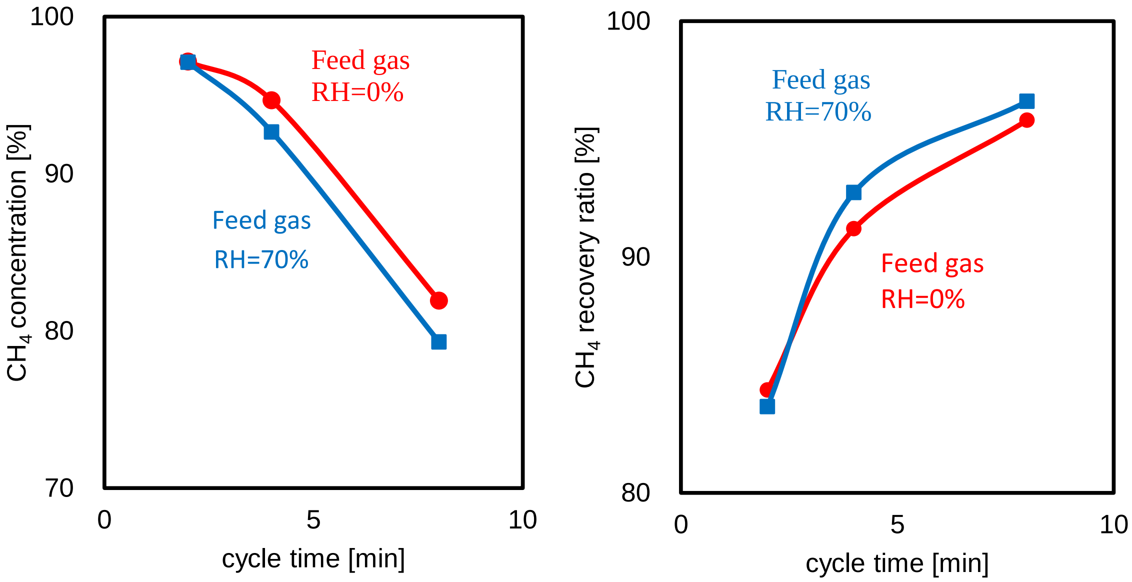


Figure 1 World CO_2 emmissions[7]

In chapter 1, background of this study is described with reviewing the related literatures. As presented in Figure 1, the world CO_2 emission increasing from the 1960s and start to decrease for about 2 decades but keep incline until today. If the emission of CO_2 continues to maintain the steady increasing rate, everyone in this planet should be concern with this situation because the trend is not expected to have any difference in short time. CO_2 that emitted today takes time to accumulate in the atmosphere and then it remains in the atmosphere for thousands of years.

In chapter 2, separation performance of simulated biogas by vacuum swing adsorption and the influence of the coexistence of water vapor in the feed gas were mainly discussed. In addition to the measurement of adsorption breakthrough curve, PSA cycle operation was carried out changing important variables which are cycle times, desorption pressure, water vapor content in the feed gas. Also, time profile of temperature distribution developed in the adsorption column was measured in order to observe a simultaneous heat and mass transfer in the column. As adsorbents, Zeolite 13X, which has satisfactory adsorption ability for CO_2 and the carbon molecular sieve (CMS), which is a hydrophobic adsorbent, were employed. The experimental results show that biogas separation performance and water vapor influence are greatly affected by cycle time and desorption pressure. The recovery ratio is low if the cycle time is short, but even if the desorption pressure is increased, the CH_4 concentration remain constant. In contrast, longer cycle time produced low CH_4 concentration although the recovery ratio was high. This indicates that longer cycle time makes the adsorption capacity per unit time lower. Consequently, simultaneous achievement of higher concentration and recovery ratio of CH_4 in the product gas is required.



(a) CH_4 concentration [%] (b) CH_4 recovery [%]

Figure 2 Influence of cycle time on CH_4 and recovery ratio on dry and humidified conditions (Desorption pressure 5kPa)

It was found that the separation performance of zeolite 13X significantly decreased when water vapor was contained in the simulated biogas. CMS showed no separation performance decay even though the water vapor was contained in mixed gas since the amount of adsorbed water onto the CMS was low. In this experiment, CMS adsorbent is not critically affected by the influence of water vapor. However, temperature distribution along the column shows that gas with 70% of RH is adsorbed mainly at the bottom of the column. Therefore, pre-dehumidification must be essential to improve concentration and recovery of CH_4 in the product gas, even for a PSA process employing a hydrophobic adsorbent such as CMS.

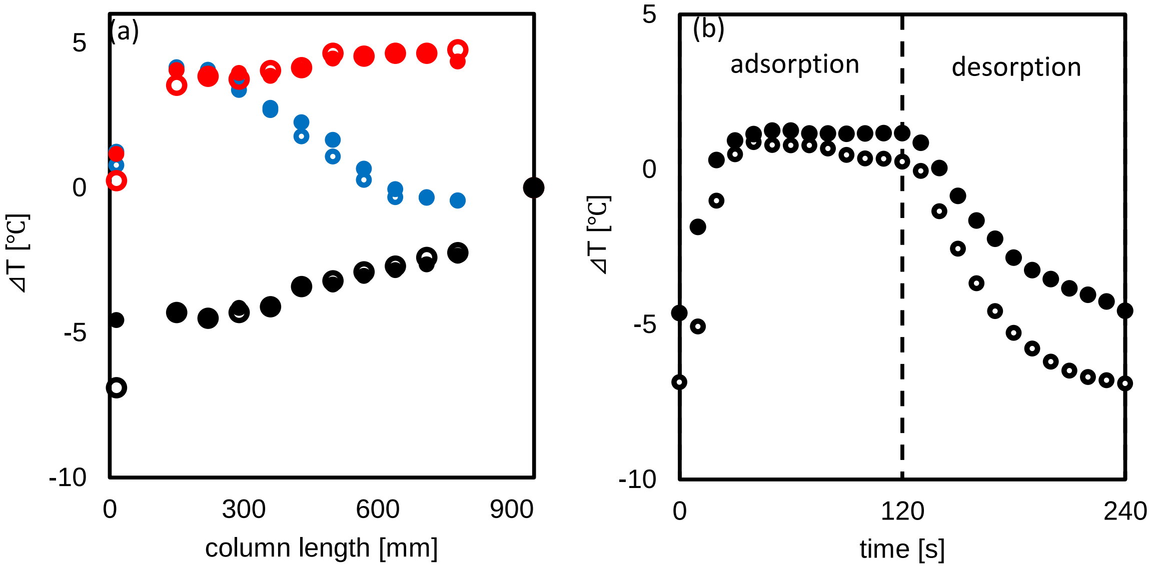


Figure 3 Temperature distributions in adsorption column for one cycle (cycle time 4 min, des pressure 15 kPa)

In chapters 3 and 4, thermal swing adsorption (TSA) using a heat exchanger packed with an adsorbent material was examined as a means of removing CO_2 from a simulated biogas. The apparatus used as shown in figure 4 where the differences between dry and humid condition is the addition of water tank is the red dash box. TSA driven by low-temperature waste heat or solar energy represents an environmentally-friendly gas separation process. In this process, the adsorbent material can be heated indirectly by circulating hot water through a heat exchanger and can operate with a smaller amount of regeneration air than in a conventional TSA system to significantly increase the CO_2 concentration at the regeneration outlet. In the present work, carbon molecular sieves (CMS) and a high-silica zeolite (HSZ) were examined with regard to their CO_2 adsorption from a simulated biogas containing 60% CH_4 and 40% CO_2.

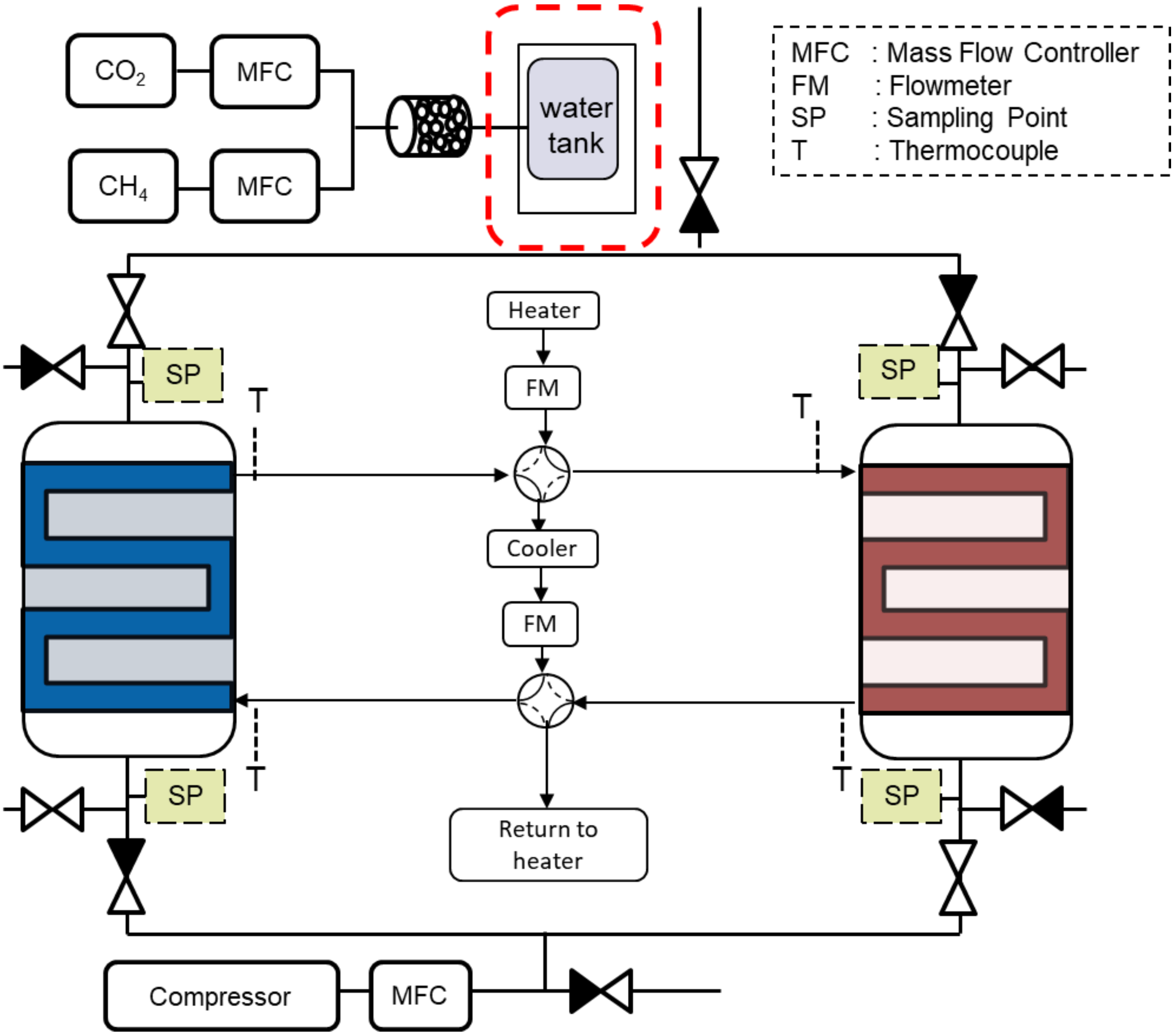


Figure 4 The TSA apparatus, incorporating two heat exchangers with water tank

The results shown in figures 5-9 are comparison between dry and humid condition with variable experiment condition. Experimental condition applied for this experiment is explained in table 1. The effects of the hot water temperature supplied to the adsorber and the regeneration air flow rate on the separation performance were investigated. Increasing the regeneration temperature was found to improve the separation performance, and the HSZ was observed to be more selective for CO_2 during the adsorption process. However, the CO_2 concentration in the desorption outlet gas was not increased when the regeneration air flow was equal to that of the feed gas. Reducing the regeneration air flow rate to one tenth the original value significantly increased the CO_2 concentration at the desorption outlet while only slightly lowering the CH_4 concentration in the product gas. A TSA process incorporating an adsorbent-packed heat exchanger is evidently an effective means of processing biogas, based on poor adsorption of CH_4 and strong adsorption of CO_2. The same experiments were repeated under the humid feed condition in order to investigate the influence of water vapor on the separation performance.

Table 1 Experimental condition

Step	Gas [vol%]	Flow rate [NL/min] (Space velocity [min^{-1}])	Temperature [°C]	Half cycle time [min]	Relative Humidity [%]
Adsorption	CH_4 : 60 CO_2 : 40	1.0 (4.4)	20	6	70 ± 5
Desorption	Dry Air	0.1, 0.3, 0.7,1.0	80		0

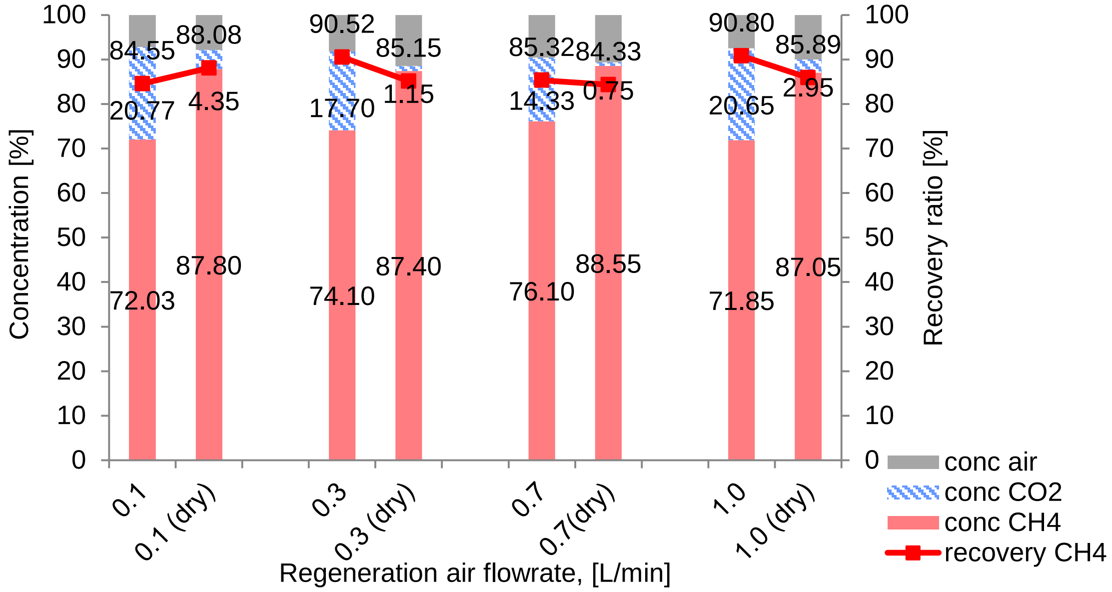


Figure 5 CH_4 and CO_2 Concentrations and CH_4 Recovery Ratio at the adsorption outlet of HSZ column

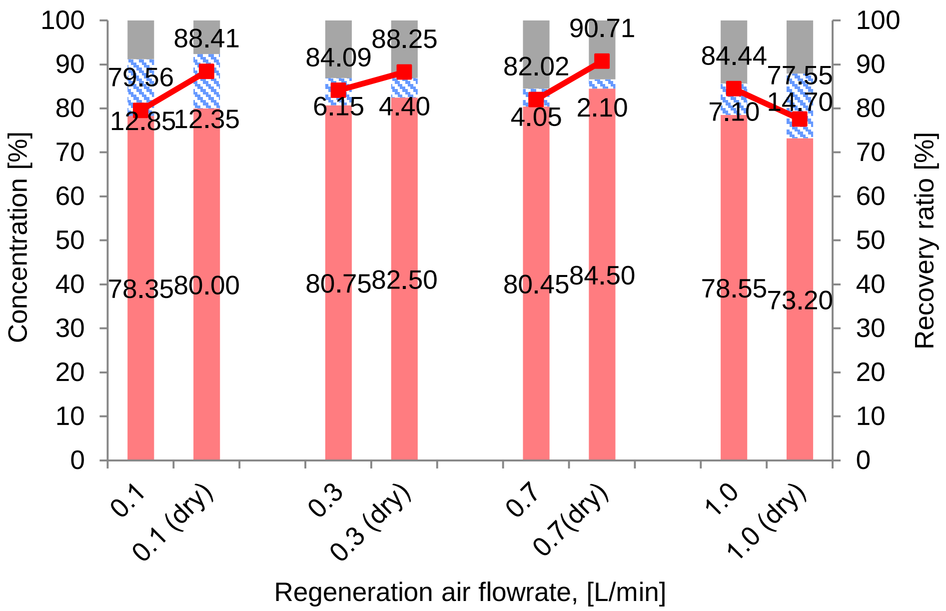


Figure 6 CH_4 and CO_2 Concentrations and CH_4 Recovery Ratio at the adsorption outlet of CMS column

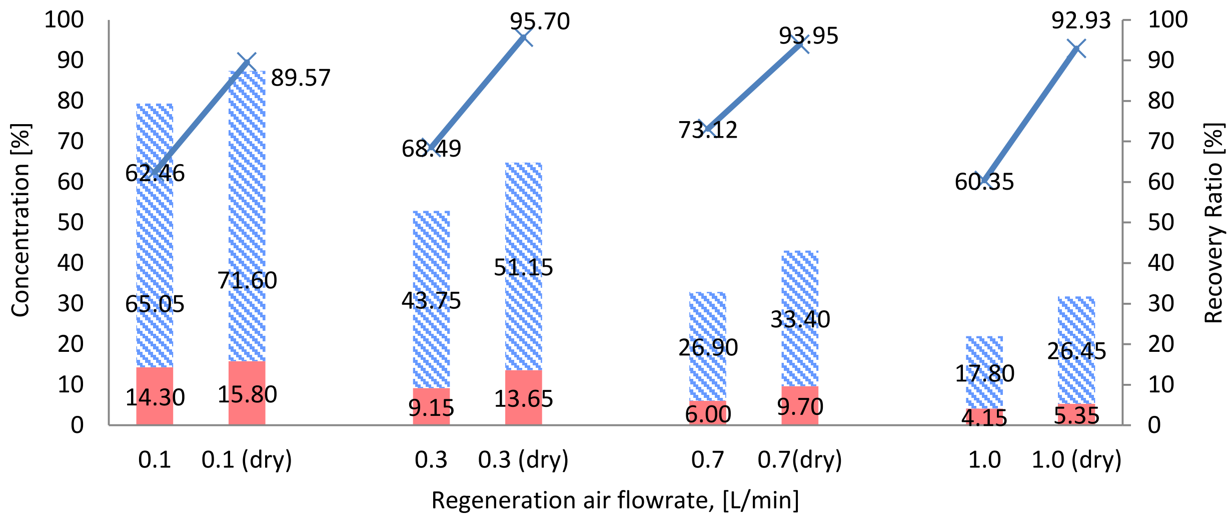


Figure 7 CH_4 and CO_2 Concentrations and CO_2 Recovery Ratio at the desorption outlet of HSZ column

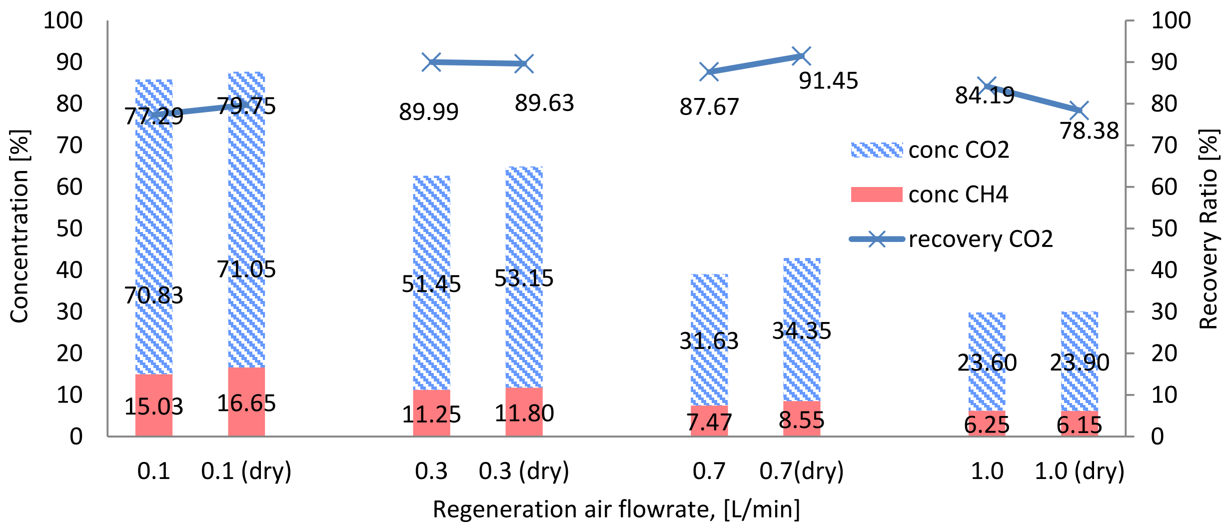


Figure 8 CH_4 and CO_2 Concentrations and CO_2 Recovery Ratio at the desorption outlet of CMS column

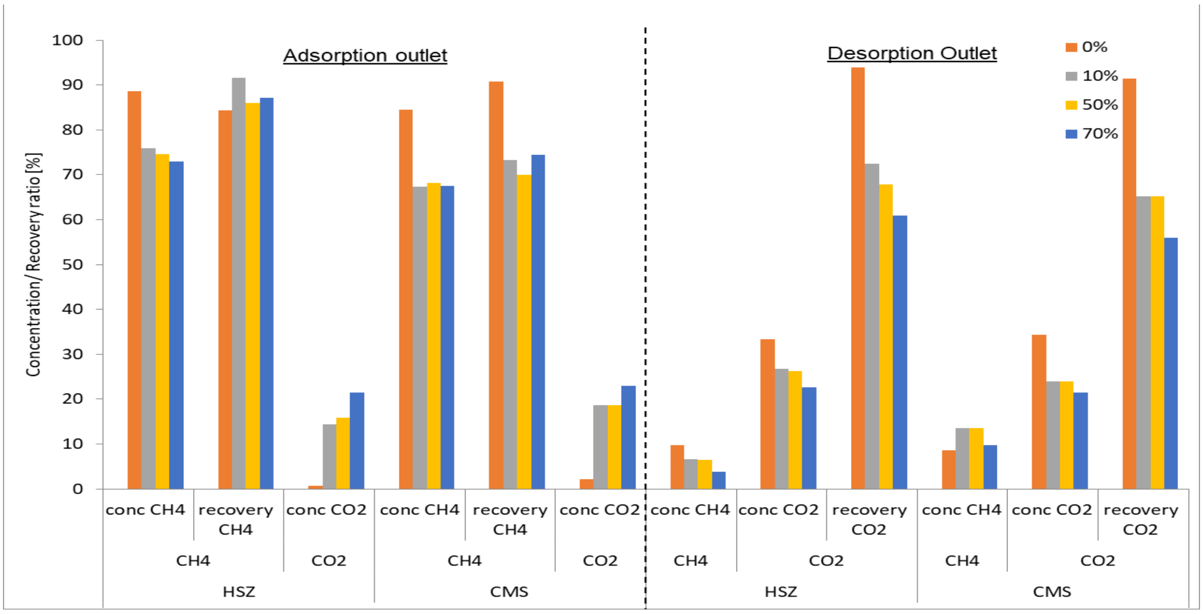


Figure 9 Influence of relative humidity at feed gas on the separation performance (0.7L/min, 6min, RH 0, 30, 50, 70%)

As for the conclusion, by comparing the results to dry feed condition, it was obviously proven that the composition of product and desorption outlet gas were affected by humidity feed gas as well as PSA described in Chapter 2. It was also confirmed that a hydrophobic adsorbent, CMS, indicated a better separation performance for the feed with humidity.

平成３１年　２月　５日

学位論文審査報告書（甲）

１．学位論文題目（外国語の場合は和訳を付けること。）

Study on Adsorptive Separation Processes for CH_4 Enrichment and CO_2 Recovery from Biogas

（バイオガス中メタンの濃縮および二酸化炭素回収のための吸着分離プロセスに関する研究）

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３．審査結果の要旨（600～650字）

当該学位論文に関し，平成31年2月4日に第1回学位論文審査委員会を開催し，提出された学位論文および関係資料について詳細に検討した。さらに，翌2月5日に行われた口頭発表後に第2回学位論文審査委員会を開催し，慎重に協議した結果，以下の通り判定した。

本論文は，周期的吸脱着操作によるバイオガス中 CO_2 と CH_4 の分離・同時濃縮の可能性および共存水蒸気の影響を明らかにしたものである。特に温度スイング吸着プロセスのパージレス化，すなわち脱着促進ガスの少量化による強吸着質（CO_2）の濃縮回収に特徴を有し，パージレス化の手法として吸着材の熱伝導加熱を可能とする吸着材充填熱交換器を提案している。CO_2 吸着材として分子ふるい炭素とハイシリカゼオライトを用いた実験を行い，脱着促進ガス流量が分離対象バイオガス流量の 1/10 であっても温度スイング操作は可能であり，脱着回収される CO_2 濃度は80%を超え，さらに脱着初期の CO_2 濃度は90%に達することを明らかにした。また，バイオガスに含まれる水蒸気の影響を調べ，低い相対湿度域から良好な水蒸気吸着特性を示すハイシリカゼオライトでは水蒸気の吸脱着量が大きく，CO_2 に対する吸着能が低下することを確認，疎水性である分子ふるい炭素の優位性を述べた。

以上，本論文は，周期的吸脱着操作によるバイオガスの分離濃縮に関し，実験を通じて学術的かつ工学的に有用な知見を得ており，博士（学術）の学位に値するものと判定した。

４．審査結果　(1) 判　定（いずれかに○印）　合　格　・　不合格

(2) 授与学位　博　士（学　術）